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Separation of Calcium in Solutions of High Sodium Content & Its Determination by Flame Photometry

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A method is described for the flame photometric determination of 2-50 ppm of calcium in solutions containing up to 4% of sodium. The calcium is concentrated on a column of Dowex A-1 chelating resin (Na^+ - form), sodium being eluted with a solution of hydrochloric acid at *p*H 2.4.

Williams and Pennington[1] have shown that ion exchange resins containing chelating groups have marked selectivity for complex-forming cations. Olsen, *et al.*[2] described the use of the ion exchange resin, Dowex A-1 in the determination of calcium in lithium salts. Van der Reyden and Van Lingen[3] reported a titrimetric method for the determination of calcium in microgram amounts in commercial sodium hydroxide solutions using this resin. In the present method, we have employed a combination of ion exchange separation of calcium from solutions of high sodium content and its determination by flame photometry up to 50ppm in such solutions.

Deionised conductivity water was used for preparing working solution of sodium chloride(AR) and calcium carbonate (AR). Standard calcium solution was prepared by dissolving calcium carbonate in the minimum amount of hydrochloric acid.

*p*H measurements were made using a Cole-Parmer instrument (Cole-Parmer, Chicago) with SCE as a reference electrode.

Flame photometric measurements were carried out on a Corning 400 (Corning, England) flame photometer using a compressed air-butane flame. Calibration curves were plotted for 0-10ppm calcium and 0-100ppm of sodium.

The ion exchange resin, Dowex A-1, in the sodium form was used. The effect of sodium and hydrochloric acid on the emission from solutions containing various concentrations of calcium was examined. On a typical calcium solution containing 5ppm calcium it was found that to obtain a reading within 5% of the true calcium value the sodium content of the solution must be less than 15ppm and the solution should be 0.12*M* in HCl.

The effect of column size, flow rate, *p*H etc., on the elution behaviour of sodium and calcium was studied. In the first set of experiment Dowex A-1 (sodium-form) (5g) was slurried into a column (int. diam. = 1cm; length = 11cm) and a solution containing 40ppm of calcium passed through the column. The effect of *p*H of the eluting solution on the sodium and calcium content of the effluent was studied by passing the solution (100ml) of known *p*H down the column at a flow rate of 1ml/min (this flow rate was maintained throughout the investigation). Aliquots of the effluent were collected and the sodium and calcium content measured by flame photometry. The remaining cations were stripped from the column using 2*M* hydrochloric acid (50ml). Successive aliquots of this effluent were analysed as before.

The sodium and calcium contents of the effluent were plotted against the volume of the eluting solution and the resulting curves (Fig. 1) showed little change when the *p*H of the eluent was varied in steps of one *p*H unit from 7 to 3. It should be pointed out that the calcium values in these results were not absolute concentrations, due to the presence of sodium, which gave a continuous background reading (equivalent to 0.5 to 2.0 ppm of calcium) on which the calcium elution peak was superimposed. Figure 1 indicated that at the *p*H studied, sodium was slowly eluted but not effectively released.

The calcium-resin complex was unaffected. Elution with a large volume of solution at *p*H 2 showed that sodium was continuously removed but that calcium did not appear in the effluent until 300ml had been collected (Fig. 2) emphasizing the very strong affinity of the resin for calcium. These results suggested that

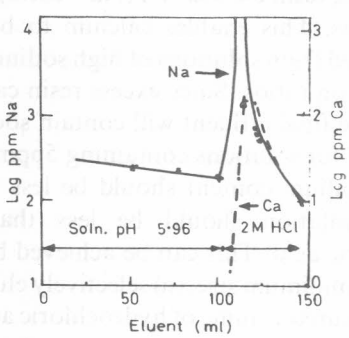

Fig. 1—Typical curve showing the variation of sodium and calcium content of effluent (*p*H of eluent was varied in step of 1 *p*H unit from 7 to 3)

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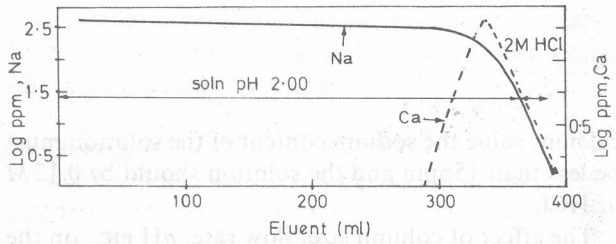

Fig. 2—Elution of column with large volume of eluent at *p*H 2 (sodium continuously removed but calcium did not appear in the effluent until 300 ml had been collected)

the diameter of the column might be reduced with no loss of calcium but with a large reduction in sodium retention. Since Fig. 2 suggested some chromatographic separation, the column of 4mm internal diameter but of same length (11cm) was used; the other experimental conditions remaining the same as above. Elution with solutions of *p*H varying from 3 to 2 in 0.2 *p*H steps showed that at *p*H = 2.44 all the sodium and almost no calcium was removed.

Yet in another experiment a solution (100ml) containing 2 to 10ppm of calcium and 4% sodium was passed down the column (int. diam. = 3mm and length = 11cm) containing 0.3g (dry weight) of sodium-form of the resin at a flow rate of 1ml/min. Sodium was eluted with 120ml of hydrochloric acid at *p*H 2.4 and the effluent discarded. Calcium was stripped from the column using 2*M* HCl (5ml) followed by deionised water (25ml). The combined effluent and washings were made up to 100ml and the calcium content determined by flame photometry.

The results obtained on a column with int. diam. = 4mm and length = 11cm and containing 0.5g of the resin (Na^+-form) are presented in Table 1. It was found that for solutions containing 10-25ppm and 24-50ppm of calcium, and each with 4% sodium, the sodium was eluted out with 200ml and 150ml respectively of 2*M* HCl at *p*H 2.4.

The results of the experiments given in Table 1, show that calcium ions are absorbed much more strongly by the chelating resin Dowex A-1 (Na^+-form) than are the sodium ions. This enables calcium to be selectively concentrated from solutions of high sodium to calcium concentration ratios. Since excess resin capacity must be used, the final effluent will contain sodium. It was shown that for solutions containing 5ppm of calcium, the final sodium content should be less than 25ppm and the solution should be less than 0.1*M* in hydrochloric acid. This can be achieved by (i) using a column of minimum size, (ii) selectively eluting sodium with a measured volume of hydrochloric acid at *p*H 2.4 and (iii) using the minimum volume of 2*M* hydrochloric acid to strip calcium from the resin. Each of these variables must be related to the composition of the original solution. The optimum values of (i) and (ii) above for particular solutions are given in Table 1.

Table 1—Determination of Calcium in Solutions Containing 2-50ppm of Calcium and 4% Sodium

[Column size: int. diam. = 4mm; length = 11cm; amount of resin (Na^+-form) = 0.5g (dry weight); eluent = 120-200ml of HCl (*p*H = 2.4)]

Calcium(ppm)			S.D.
Added	Blank	Found*	
2.0	0.70	2.3	0.19
4.0	0.70	3.96	0.21
6.0	0.50	5.84	0.19
8.0	0.50	7.86	0.19
10.0	0.55	9.97	0.16
15.0	0.60	14.92	0.20
20.0	0.50	20.24	0.14
25.0	0.60	25.04	0.17
40.0	0.60	39.98	0.15
50.0	0.65	50.01	0.14

*Mean of five runs.

In all the cases, calcium was stripped with 5ml of 2*M* hydrochloric acid, the column washed with deionised water and the effluent and washings diluted to 100ml, thus reducing the acid concentration to less than the critical value.

The results showed a positive deviation without blank values of calcium being substracted. However, the blank values obtained from set to set was substracted in the values recorded in Table 1. Statistical analysis of calcium concentrations in the 0-50ppm range show that the deviations were insignificant. The blank values of calcium varied between 0.50 and 0.70ppm. This is within the limits of experimental error. Hence, this does not necessarily reflect a variable sorption of calcium under the experimental conditions.

Heavy metals present singly at a concentration of 25ppm or collectively at a concentration of 5ppm each, do not interfere in the determination of calcium in solutions containing 2-4% of sodium. However, it is observed that aluminium interferes in the determination of calcium.

References

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